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ABSORPTION BAND SPECTRA OF
CARBON DISULPHIDE, IODINE MONOCHLORIDE
AND THE HYDROXYL RADICAL

DISSERTATION

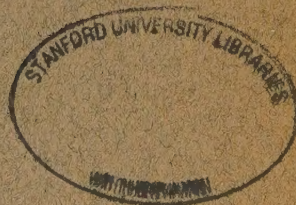
PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE
SCHOOL OF THE OHIO STATE UNIVERSITY

BY

EARL DEWITT WILSON, B. A., M. A.

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THE ABSORPTION SPECTRUM OF CS_2 IN THE NEAR ULTRA-VIOLET

EARL D. WILSON

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THE ABSORPTION SPECTRUM OF CS_2 IN THE NEAR ULTRA-VIOLET

By EARL D. WILSON

ABSTRACT

The absorption spectrum of carbon disulphide vapor in the near ultra-violet has been photographed under varied experimental conditions in such a manner as to exhibit a rather complete development of the band system *over the range of wave-lengths λ 2900– λ 3800.*

The wave-lengths of about 650 *absorption lines* have been *measured*, and their *relative intensities estimated from photometric curves.*

Certain regularities of structure in the band system have been pointed out, and some series with constant differences in frequency recorded.

INTRODUCTION

For more than a quarter of a century investigators have been baffled by the intricacy of the molecular spectra of the familiar compound, carbon disulphide. Only meager data have been published up to the present time, so that it is necessary for each new investigator to begin all the work afresh.

The work of W. W. Coblentz,¹ which compares the infra-red emission spectrum of burning CS_2 with the absorption spectrum of the liquid phase, constitutes about all of the data available in the region of long wave-lengths. Covering the spectral region from $2\ \mu$ to $15\ \mu$, he records only the three absorption bands at $4.6\ \mu$, $6.75\ \mu$, and $11.65\ \mu$, although his own curve indicates the presence also of other bands at $3.2\ \mu$, $6.3\ \mu$, and $13.4\ \mu$.

More than fifty years ago Liveing and Dewar² investigated in a qualitative manner the absorption spectra of a number of gases and vapors. They found bands for CS_2 extending over the region from λ 3360 to λ 3020. About fifteen years later J. Pauer³ measured the wave-lengths of twenty-four members of this system. In 1919 Miss Pauly⁴ with improved apparatus succeeded in measuring as many as eighty-five lines ranging from λ 3589 to λ 2919.

Aside from measurements of absorption coefficients of CS_2 liquid

¹ *Physical Review*, **24**, 72, 1907.

² *Proceedings of the Royal Society*, **35**, 71, 1883.

³ *Annalen der Physik*, **61**, 363, 1897.

⁴ *Astrophysical Journal*, **50**, 155, 1919.

for ultra-violet light and the additional fact¹ that a second strong absorption band occurs with maximum at about λ 2200, the foregoing summarizes our present state of published knowledge concerning the molecular spectra of CS_2 .

The writer has therefore thought it worth while to investigate the near ultra-violet absorption spectrum of CS_2 vapor with the aid of modern equipment in order that data of wave-lengths and intensities might be prepared more adequate to ultimate quantum analysis.

EXPERIMENTAL PROCEDURE

The carbon disulphide used in this investigation was chemically pure, being colorless and having no unpleasant odor. The vapor was confined in a glass tube with end plates of fused quartz secured in position by an acetic-acid-gelatine cement. Liquid, introduced through a side tube, occupied a bulb attached to the opposite wall of the vapor chamber. The bulb was provided with a long stem to facilitate its immersion in a bath of desired temperature. Other side tubes made possible the evacuation of the system or the circulation of vapor. Five such vapor chambers, ranging in length from 2 to 60 cm, provided convenient means of varying the length of the column of vapor.

The under-water spark was employed as a source of continuous radiation in the ultra-violet. For preliminary determination of the conditions most suitable for developing the band system *in extenso*, a Fery spectrograph of small dispersion (roughly 40 Å per mm in ultra-violet) was found quite expedient. A series of photographs of the absorption spectrum was made, varying successively the different disposable parameters of the equipment. The length of vapor column was varied by substituting different vapor chambers. The vapor pressure was altered either by use of a vacuum pump or by changing the temperature of the bath in which the bulb was immersed. It so happens that the freezing point of CS_2 is extremely low, -110° C., and the liquid could be readily frozen by its own evaporation at low pressure. The vapor pressure of the ice was so low that no absorption occurred. Other temperatures were secured by salt and ice baths and by baths of water warmed stepwise from

¹ Bruhat and Pautheimer, *Comptes rendus*, **179**, 154, 1924.

0° to 100° C. At these higher temperatures, the chamber was wrapped in asbestos paper and warmed with Bunsen flames so that no condensation of CS_2 vapor could take place on the end plates. Pressures as high as 3 or 4 atm. were obtained in this manner, as estimated by consulting Regnault's tables for the vapor pressure of CS_2 at various temperatures.

Such experiments showed: first, that the structure of the band system did not depend critically either upon the temperature in itself or upon the pressure of air or upon the length of exposure; second, that the intensity of the system was a consistent function of the number of molecules traversed by the incident radiation, by whatever means this number was varied.

The conditions suitable for the absorption of the bands having been determined, the significant exposures were repeated with a Hilger E-1 spectrograph. The arc spectrum of iron was used as a standard of wave-length.

By means of a Moll microphotometer, intensity-curves both of the CS_2 -absorption lines and iron-emission lines were traced successively upon the same print. Altogether, eight final prints were completed which faithfully portrayed the structure of the system in overlapping portions from λ 3800 to λ 2900. Figure 1 is a copy (with iron lines omitted) of one of the prints for the central, most intense portion of the band system. Figure 2 represents the least refrangible portion of the whole band system.

The wave-lengths of about six hundred and fifty absorption lines were measured partly from these photometer prints and partly from the original plates. The results are recorded in Table I. The error to be expected is of the order of 0.05 Å, as judged from overlapping sections from separate plates.

The relative intensities of the lines were estimated linearly from the corresponding amplitudes on the photometric curves. The weakest lines are counted unity; and the line of maximum intensity, 1000 units.

Discussion of structure of the band system.—In general, the intensity of the system is greatest in the central portion, decreasing with some uniformity toward both longer and shorter wave-lengths. By far the most intense bands are included in the range between

about λ 3100 and λ 3300. In this region there are numerous maxima of intensity having values of the order of 300 to 1000. At λ 3275 there is a sudden decrease from an intensity of about 750 to those of value about 150, and after the group of lines at λ 3320 the intensities decrease rapidly from about 30 or 40 to unity. On the more refrangible side, the decrease of intensity proceeds without any unusual discontinuities.

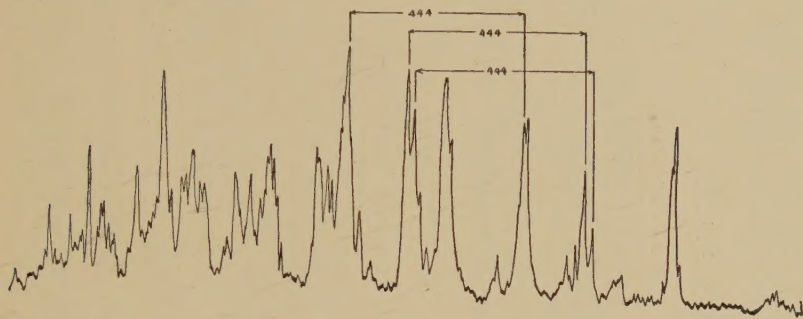


FIG. 1.—Photometer-curve of the central part of the CS_2 band system

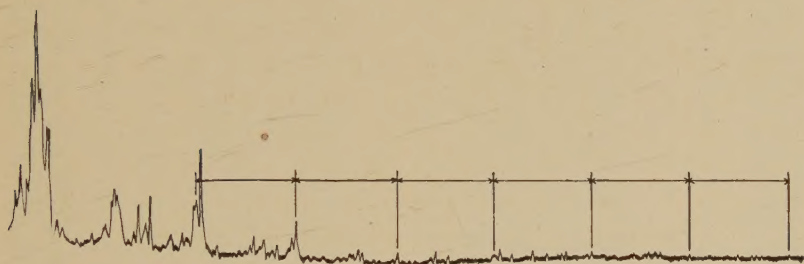


FIG. 2.—Photometer-curve of the long-wave part of CS_2 band system

It is a very noticeable fact that the more refrangible end of the system is much less sharply defined than the end of longer wave-lengths. Also no standard band structure is evident, but the appearance is more suggestive of a mixture of resolved and unresolved atomic lines.

Certainly there are very few obvious regularities in frequency-differences in the CS_2 absorption spectrum. Perhaps the series that appear most promising under low dispersion are those extending to longer wave-lengths from the neighborhood of λ 3275. Under higher dispersion, the members of the series are composed each of a number

TABLE I

ABSORPTION BANDS OF CS₂ IN NEAR ULTRA-VIOLET

λ (I.A.)	I	ν (Vac.)	λ (I.A.)	I	ν (Vac.)	λ (I.A.)	I	ν (Vac.)
2007.30.....	2	34386.1	2060.16.....	5	33772.1	3022.78.....	100	33072.5
2008.10.....	3	34376.7	2060.42.....	5	33769.2	3023.99.....	100	33059.2
2008.57.....	4	34371.1	2061.53.....	1	33756.5	3024.97.....	80	33048.6
2009.37.....	5	34361.7	2062.16.....	1	33749.3	3025.73.....	36	33039.3
2009.83.....	5	34356.2	2063.77.....	8	33731.0	3026.99.....	36	33026.4
2010.40.....	5	34349.5	2064.63.....	10	33721.2	3027.32.....	43	33022.9
2011.58.....	8	34335.6	2065.02.....	20	33716.8	3027.77.....	55	33018.0
2012.40.....	9	34325.9	2065.78.....	16	33708.1	3028.24.....	70	33012.9
2013.41.....	9	34314.0	2066.35.....	23	33701.7	3028.85.....	33	33006.3
2013.88.....	6	34308.5	2067.66.....	23	33686.8	3029.63.....	33	32997.7
2014.39.....	5	34302.5	2068.02.....	20	33682.7	3030.11.....	40	32992.4
2015.33.....	4	34291.4	2069.02.....	13	33671.3	3031.74.....	65	32974.8
2015.79.....	5	34286.0	2069.32.....	10	33667.0	3032.28.....	75	32968.9
2017.24.....	4	34269.0	2070.55.....	23	33654.0	3033.33.....	120	32957.5
2017.59.....	4	34264.0	2071.05.....	33	33648.3	3034.27.....	120	32947.3
2018.18.....	3	34257.0	2072.98.....	23	33626.5	3036.40.....	120	32924.2
2019.36.....	4	34244.1	2073.82.....	26	33617.0	3037.29.....	75	32914.5
2020.36.....	4	34232.4	2074.48.....	20	33609.5	3038.22.....	110	32904.4
2020.90.....	4	34226.0	2075.14.....	10	33602.1	3038.70.....	90	32899.3
2021.51.....	3	34218.0	2076.15.....	7	33590.7	3039.68.....	80	32888.6
2022.48.....	5	34207.5	2077.28.....	20	33577.9	3041.08.....	70	32873.5
2022.84.....	5	34203.3	2077.69.....	23	33573.3	3042.25.....	33	32860.9
2023.97.....	8	34199.1	2078.55.....	26	33563.6	3043.88.....	23	32843.3
2024.33.....	10	34185.9	2079.33.....	40	33554.8	3044.80.....	36	32833.4
2024.93.....	8	34178.9	2080.6.....	10	33541	3045.46.....	33	32826.2
2025.67.....	8	34170.2	2082.40.....	7	33520.3	3046.88.....	23	32810.9
2026.19.....	5	34164.2	2082.98.....	10	33513.8	3048.90.....	50	32789.2
2027.15.....	2	34153.0	2083.23.....	12	33511.0	3049.72.....	50	32780.4
2028.16.....	4	34141.2	2083.53.....	13	33507.6	3050.76.....	80	32769.2
2028.60.....	4	34136.0	2084.59.....	22	33496.7	3051.74.....	80	32758.7
2029.11.....	4	34130.1	2085.26.....	30	33488.2	3052.33.....	75	32752.4
2029.82.....	4	34121.8	2085.70.....	23	33483.2	3053.23.....	55	32742.7
2030.81.....	6	34110.3	2086.74.....	10	33471.6	3054.41.....	40	32730.0
2031.40.....	6	34103.4	2087.72.....	4	33460.6	3055.33.....	50	32720.2
2031.93.....	6	34098.4	2089.07.....	10	33445.5	3056.32.....	80	32709.6
2032.92.....	8	34086.9	2090.32.....	16	33431.5	3056.83.....	100	32704.1
2033.60.....	9	34077.9	2091.48.....	43	33418.5	3057.87.....	43	32693.0
2033.95.....	10	34073.8	2092.77.....	55	33404.1	3058.71.....	20	32684.0
2034.80.....	7	34063.9	2093.44.....	05	33397.6	3059.70.....	10	32673.5
2035.27.....	7	34058.5	2094.05.....	06	33389.9	3060.75.....	13	32662.3
2035.95.....	5	34050.6	2095.15.....	16	33377.0	3061.14.....	10	32658.1
2037.32.....	7	34034.7	2096.36.....	7	33364.1	3062.18.....	7	32647.0
2038.19.....	8	34024.6	2097.50.....	13	33351.4	3063.81.....	23	32629.6
2038.92.....	5	34016.2	2098.36.....	16	33341.9	3064.32.....	36	32624.2
2039.62.....	2	34008.1	2099.60.....	10	33328.1	3065.02.....	23	32616.7
2041.13.....	2	33990.6	3000.46.....	4	33318.6	3065.83.....	27	32608.1
2041.96.....	1	33981.0	3001.15.....	4	33310.0	3067.34.....	43	32592.1
2042.23.....	1	33977.9	3001.70.....	7	33304.8	3068.25.....	75	32582.4
2042.80.....	2	33971.3	3002.97.....	10	33290.7	3068.63.....	75	32578.4
2043.17.....	3	33967.1	3003.23.....	10	33287.8	3069.05.....	80	32574.1
2044.20.....	3	33955.2	3004.42.....	7	33274.6	3070.82.....	120	32555.1
2045.19.....	8	33943.8	3005.19.....	5	33266.1	3072.23.....	185	32540.2
2045.83.....	10	33936.4	3006.13.....	13	33255.7	3073.14.....	160	32530.6
2046.14.....	10	33932.8	3006.90.....	13	33247.2	3074.13.....	90	32520.1
2046.60.....	8	33926.5	3007.77.....	23	33237.6	3074.99.....	100	32510.9
2047.60.....	6	33916.0	3008.46.....	23	33229.9	3077.01.....	145	32489.7
2048.60.....	9	33904.5	3008.65.....	43	33227.8	3078.17.....	145	32477.4
2049.52.....	6	33893.9	3009.44.....	60	33219.1	3079.39.....	120	32464.6
2050.40.....	10	33883.8	3010.60.....	13	33206.3	3080.14.....	240	32456.7
2051.08.....	7	33876.1	3011.67.....	20	33194.5	3080.66.....	360	32451.2
2052.00.....	10	33865.5	3012.01.....	20	33190.8	3080.99.....	290	32447.6
2052.90.....	16	33855.1	3013.09.....	43	33178.9	3082.18.....	225	32435.2
2053.96.....	7	33843.0	3014.31.....	27	33165.4	3083.32.....	135	32423.2
2054.50.....	8	33836.8	3015.08.....	50	33157.0	3084.34.....	135	32412.5
2055.35.....	7	33827.1	3017.00.....	43	33135.9	3085.97.....	170	32404.8
2056.07.....	5	33818.8	3018.35.....	13	33121.1	3085.86.....	105	32396.5
2056.68.....	4	33811.9	3019.38.....	33	33109.8	3087.30.....	305	32381.4
2058.20.....	6	33794.5	3019.95.....	36	33103.5	3088.23.....	120	32371.6
2058.82.....	8	33787.4	3020.73.....	46	33094.9	3089.85.....	65	32354.7
2059.33.....	10	33781.6	3022.10.....	65	33080.0	3091.66.....	305	32335.7

TABLE I—Continued

λ (I.A.)	I	ν (Vac.)	λ (I.A.)	I	ν (Vac.)	λ (I.A.)	I	ν (Vac.)
3092.49.....	475	32326.9	3153.96.....	410	31697.0	3231.82.....	265	30933.4
3092.99.....	475	32321.7	3154.42.....	395	31692.4	3233.4.....	410	30918
3093.51.....	290	32316.5	3155.7.....	36	31680	3234.50.....	760	30907.8
3094.07.....	90	32304.3	3157.07.....	65	31665.8	3235.28.....	760	30900.3
3095.88.....	170	32291.6	3157.58.....	65	31660.7	3236.84.....	130	30885.4
3096.82.....	160	32281.8	3158.59.....	110	31650.6	3237.90.....	55	30875.3
3097.78.....	145	32271.8	3159.4.....	175	31642	3238.04.....	26	30868.3
3099.11.....	160	32258.0	3160.1.....	145	31635	3239.80.....	26	30857.2
3099.79.....	290	32250.8	3161.05.....	330	31625.9	3240.68.....	13	30848.8
3100.30.....	360	32244.6	3161.50.....	365	31621.4	3242.34.....	26	30833.0
3100.83.....	280	32240.1	3161.94.....	425	31617.0	3243.5.....	40	30822
3102.41.....	185	32223.7	3162.90.....	290	31607.0	3244.4.....	80	30813
3103.28.....	145	32214.6	3163.97.....	210	31596.7	3245.70.....	185	30801.1
3104.75.....	27	32199.4	3165.24.....	450	31584.1	3246.65.....	105	30792.1
3105.43.....	27	32192.3	3166.56.....	200	31570.9	3247.88.....	325	30780.5
3105.98.....	27	32186.6	3167.71.....	330	31559.4	3249.61.....	280	30764.1
3106.64.....	13	32179.8	3168.80.....	370	31548.6	3250.18.....	320	30758.4
3107.37.....	27	32172.2	3169.67.....	500	31539.9	3250.50.....	460	30755.1
3109.25.....	90	32152.8	3170.25.....	585	31534.1	3252.42.....	395	30737.5
3110.40.....	40	32140.9	3171.08.....	460	31525.9	3255.42.....	40	30709.2
3112.20.....	65	32122.3	3171.98.....	330	31516.0	3255.98.....	65	30703.9
3112.82.....	65	32115.9	3172.89.....	130	31507.9	3257.60.....	80	30688.6
3113.62.....	65	32107.7	3173.83.....	36	31498.6	3258.28.....	105	30682.2
3114.26.....	55	32101.1	3174.4.....	36	31493	3259.50.....	105	30670.7
3114.97.....	90	32093.7	3175.20.....	55	31485.0	3260.42.....	130	30662.1
3115.45.....	90	32088.8	3176.28.....	26	31474.3	3261.93.....	22	30647.9
3116.27.....	175	32080.3	3177.12.....	55	31466.0	3262.72.....	30	30640.5
3117.07.....	345	32072.1	3178.30.....	13	31454.3	3263.75.....	48	30630.8
3117.60.....	175	32065.7	3179.43.....	55	31443.1	3264.79.....	48	30621.0
3118.57.....	175	32056.7	3180.53.....	185	31432.2	3265.50.....	33	30614.4
3119.30.....	530	32049.2	3181.51.....	595	31422.6	3266.12.....	30	30608.6
3120.11.....	145	32040.9	3182.2.....	545	31416	3267.37.....	43	30596.9
3121.02.....	105	32031.6	3184.18.....	500	31396.2	3268.39.....	40	30587.3
3122.15.....	305	32019.9	3185.33.....	435	31384.9	3269.58.....	30	30576.2
3123.12.....	175	32010.0	3185.87.....	300	31379.5	3270.38.....	41	30568.7
3123.43.....	160	32006.8	3186.65.....	495	31371.9	3271.53.....	65	30558.0
3124.43.....	185	31996.5	3187.46.....	665	31363.9	3274.06.....	565	30534.3
3124.96.....	200	31991.2	3188.11.....	790	31357.5	3274.77.....	745	30527.7
3126.61.....	595	31974.3	3189.49.....	1000	31343.9	3275.94.....	145	30516.8
3127.90.....	90	31961.1	3192.30.....	320	31316.4	3276.82.....	65	30508.6
3128.50.....	250	31955.0	3193.75.....	55	31302.1	3278.12.....	55	30496.5
3129.28.....	345	31947.0	3194.40.....	95	31295.8	3279.71.....	26	30481.9
3129.97.....	360	31940.0	3194.85.....	120	31291.3	3280.26.....	50	30476.6
3131.19.....	265	31927.5	3195.68.....	55	31283.2	3281.52.....	40	30464.9
3131.97.....	160	31919.6	3196.37.....	36	31276.5	3283.15.....	22	30449.8
3132.45.....	190	31914.7	3197.70.....	13	31263.5	3283.80.....	26	30433.8
3133.12.....	90	31907.8	3198.39.....	26	31256.8	3285.12.....	33	30431.6
3134.2.....	40	31897	3199.71.....	36	31243.8	3285.70.....	18	30426.2
3135.41.....	145	31884.5	3201.12.....	36	31230.1	3287.82.....	43	30406.5
3135.71.....	500	31881.5	3202.41.....	200	31217.5	3288.69.....	32	30398.5
3136.88.....	90	31869.6	3203.89.....	665	31203.1	3289.42.....	46	30391.8
3137.64.....	505	31861.9	3204.38.....	820	31198.3	3289.82.....	41	30388.1
3139.1.....	200	31847	3206.08.....	665	31181.8	3290.41.....	38	30382.6
3140.0.....	200	31838	3207.75.....	425	31165.5	3291.20.....	48	30375.3
3140.72.....	200	31830.6	3209.32.....	200	31150.3	3292.32.....	40	30365.0
3141.62.....	240	31821.5	3211.0.....	145	31133	3293.41.....	13	30355.0
3142.46.....	305	31813.0	3211.7.....	200	31127	3294.69.....	16	30344.0
3143.99.....	790	31797.4	3212.97.....	490	31114.0	3295.26.....	5	30337.9
3144.51.....	565	31792.3	3213.72.....	680	31107.6	3296.97.....	12	30322.2
3144.90.....	495	31788.3	3214.35.....	695	31101.5	3297.64.....	36	30316.0
3145.46.....	330	31782.7	3215.72.....	425	31088.3	3298.49.....	60	30308.3
3146.09.....	385	31776.3	3218.21.....	120	31064.2	3299.50.....	90	30298.4
3147.00.....	200	31767.1	3218.86.....	80	31057.9	3300.15.....	95	30293.0
3147.46.....	230	31762.5	3220.28.....	55	31044.2	3301.31.....	105	30282.3
3147.94.....	265	31757.6	3221.36.....	26	31033.8	3302.41.....	100	30272.2
3148.44.....	355	31752.6	3223.20.....	13	31016.1	3303.74.....	85	30260.0
3149.48.....	365	31742.1	3224.17.....	13	31006.8	3304.38.....	85	30254.2
3150.37.....	430	31733.1	3225.88.....	85	30990.3	3305.04.....	65	30248.1
3150.94.....	545	31727.4	3226.58.....	95	30983.6	3305.48.....	55	30244.1
3151.20.....	460	31724.8	3227.45.....	200	30975.3	3307.02.....	55	30230.0
3152.06.....	330	31716.1	3230.22.....	65	30948.7	3309.06.....	8	30211.4
3152.80.....	410	31708.7	3231.12.....	165	30940.1	3311.59.....	7	30203.5

TABLE I—Continued

$\lambda(\text{\AA.})$	I	$\nu(\text{Vac.})$	$\lambda(\text{\AA.})$	I	$\nu(\text{Vac.})$	$\lambda(\text{\AA.})$	I	$\nu(\text{Vac.})$
3311.93.....	7	30188.3	3402.83.....	5	20378.9	3524.14.....	I	28367.6
3314.18.....	10	30164.7	3404.10.....	6	20367.9	3524.73.....	I	28362.9
3314.69.....	8	30160.1	3404.81.....	6	20361.8	3529.73.....	I	28354.8
3315.45.....	8	30153.2	3405.70.....	7	20354.1	3525.90.....	I	28353.5
3316.96.....	18	30139.4	3407.69.....	7	20337.0	3531.54.....	I	28308.2
3318.37.....	33	30126.0	3410.18.....	3	20315.6	3533.51.....	I	28292.4
3320.46.....	120	30107.7	3412.22.....	8	20298.1	3535.23.....	I	28278.6
3321.58.....	135	30097.5	3413.56.....	8	20286.6	3536.26.....	2	28270.4
3324.96.....	85	30066.9	3415.34.....	6	20271.3	3538.05.....	I	28256.1
3326.50.....	75	30052.2	3416.14.....	8	20264.4	3539.6.....	I	28244
3327.66.....	23	30042.5	3417.13.....	7	20256.0	3540.91.....	I	28233.3
3328.93.....	13	30031.1	3417.92.....	12	20249.2	3542.61.....	I	28219.7
3329.58.....	18	30025.2	3418.48.....	12	20244.4	3544.16.....	I	28207.4
3329.91.....	16	30022.2	3419.36.....	15	20236.9	3546.00.....	I	28192.8
3330.40.....	15	30017.8	3420.76.....	7	20224.9	3548.14.....	I	28175.7
3331.10.....	15	30011.5	3423.25.....	6	20203.6	3549.28.....	I	28166.7
3333.43.....	10	29990.5	3425.21.....	3	20186.9	3550.67.....	3	28155.7
3335.10.....	8	29975.5	3427.43.....	2	20168.0	3552.20.....	I	28142.8
3335.98.....	10	29967.6	3428.90.....	4	20155.5	3554.39.....	I	28126.2
3337.15.....	20	29957.1	3430.44.....	5	20142.4	3556.26.....	I	28111.4
3338.61.....	13	29944.0	3431.54.....	4	20133.1	3559.96.....	I	28082.2
3339.76.....	18	29933.7	3432.95.....	2	20121.1	3565.17.....	I	28041.2
3341.91.....	23	29914.4	3436.19.....	13	20093.7	3566.85.....	I	28028.0
3343.07.....	26	29904.0	3437.63.....	22	20081.5	3568.0.....	I	28019
3344.01.....	22	29895.6	3439.29.....	12	20067.5	3569.15.....	I	28009.9
3345.35.....	28	29883.7	3442.00.....	5	20044.6	3570.10.....	I	28002.5
3346.04.....	36	29877.5	3444.25.....	6	20025.6	3572.00.....	I	27987.6
3347.07.....	34	29868.3	3446.00.....	2	20010.9	3573.26.....	I	27977.7
3349.01.....	26	29851.0	3447.5.....	1	28998	3574.81.....	I	27965.6
3349.98.....	15	29842.3	3449.81.....	5	28978.8	3579.30.....	I	27930.5
3350.87.....	12	29834.4	3450.84.....	5	28970.2	3583.73.....	I	27895.9
3351.52.....	8	29828.7	3452.93.....	3	28952.6	3585.62.....	I	27881.2
3352.40.....	7	29820.8	3455.52.....	1	28930.9	3587.32.....	I	27868.0
3352.98.....	5	29815.7	3459.46.....	4	28908.0	3588.32.....	I	27860.3
3354.01.....	4	29806.5	3461.17.....	5	28883.7	3589.85.....	I	27848.4
3355.35.....	8	29794.6	3463.22.....	5	28866.6	3591.95.....	I	27832.1
3356.50.....	15	29784.4	3464.92.....	12	28852.5	3597.53.....	I	27789.0
3357.42.....	23	29776.2	3466.52.....	16	28839.1	3599.14.....	I	27776.5
3358.71.....	12	29764.8	3467.46.....	12	28831.3	3600.46.....	I	27766.3
3359.82.....	5	29755.0	3469.20.....	7	28816.0	3601.58.....	I	27757.6
3360.2.....	13	29752	3469.81.....	7	28811.8	3603.59.....	I	27742.2
3361.07.....	5	29743.9	3472.40.....	2	28790.3	3621.1.....	I	27668
3361.80.....	10	29736.8	3474.14.....	1	28775.0	3622.42.....	I	27598.0
3362.65.....	12	29730.0	3475.06.....	1	28768.3	3626.72.....	I	27565.3
3363.32.....	13	29724.0	3478.45.....	1	28740.2	3634.16.....	I	27508.9
3364.09.....	20	29717.2	3480.88.....	1	28720.2	3635.52.....	I	27498.6
3366.66.....	20	29694.5	3482.00.....	1	28710.9	3639.52.....	I	27468.4
3367.40.....	20	29688.0	3482.93.....	1	28703.2	3645.12.....	I	27426.1
3369.08.....	23	29673.2	3483.53.....	1	28698.3	3646.38.....	I	27416.7
3369.79.....	23	29667.0	3484.8.....	1	28688	3654.17.....	I	27358.2
3371.42.....	13	29652.6	3485.5.....	1	28682	3650.05.....	I	27344.1
3372.80.....	5	29640.5	3486.6.....	1	28673	3659.3.....	I	27320
3373.97.....	9	29630.2	3487.57.....	2	28665.1	3660.2.....	I	27313
3376.47.....	8	29608.3	3489.52.....	3	28649.1	3664.62.....	I	27280.2
3377.41.....	6	29600.0	3490.42.....	4	28641.7	3670.03.....	I	27233.3
3378.85.....	5	29587.4	3491.43.....	4	28633.4	3671.91.....	I	27226.0
3379.97.....	1	29577.6	3492.00.....	3	28628.7	3675.88.....	I	27196.6
3380.93.....	2	29569.2	3494.82.....	1	28605.6	3677.43.....	I	27185.2
3381.76.....	5	29561.9	3496.75.....	1	28589.8	3679.98.....	I	27166.3
3382.55.....	5	29555.0	3498.04.....	3	28579.3	3681.87.....	I	27152.9
3382.91.....	5	29551.9	3500.67.....	2	28557.8	3693.14.....	I	27069.5
3384.21.....	4	29540.5	3502.26.....	4	28544.8	3711.7.....	I	26933.7
3387.52.....	7	29511.6	3503.47.....	1	28535.0	3716.07.....	I	26896.0
3388.59.....	20	29502.4	3504.00.....	1	28530.7	3718.06.....	I	26881.6
3390.80.....	20	29483.1	3504.90.....	1	28523.4	3721.14.....	I	26865.9
3392.57.....	10	29467.7	3506.02.....	1	28514.2	3731.06.....	I	26788.0
3393.36.....	10	29460.9	3509.42.....	1	28486.6	3737.6.....	I	26747
3394.66.....	15	29449.6	3512.62.....	2	28460.7	3751.5.....	I	26648
3395.18.....	7	29445.1	3513.60.....	2	28452.0	3769.8.....	I	26519
3396.71.....	7	29431.8	3514.20.....	1	28447.4	3773.0.....	I	26497
3397.67.....	8	29423.5	3516.30.....	3	28430.9	3783.9.....	I	26420
3398.45.....	4	29410.7	3517.15.....	4	28424.0	3786.11.....	I	26404.9
3399.40.....	5	29408.0	3518.04.....	6	28409.5			
3401.59.....	5	29389.6	3522.85.....	1	28378.0			

of lines. Taking one of the strongest lines from each group, we may form two possible short series:

ν	I	$\Delta\nu$	ν	I	$\Delta\nu$
30682.2.....	105	399.9	30097.5.....	135	430.5
30282.3.....	105	398.6	29667.0.....	23	430.1
29883.7.....	28	400.6	29236.9.....	15	397.8
29483.1.....	20	401.6	28839.1.....	16	429.6
29081.5.....	22		28409.5.....	6	
30527.7.....	745	430.2			

The fourth difference in the second series is entirely irregular, but the remaining values of $\Delta\nu$ are nearly enough constant to have a possible significance.

An examination of Figure 1 reveals the probable recurrence of similar groupings of lines in the intense part of the spectrum. The following frequency-differences are noteworthy:

ν_1	I	ν_2	I	$\nu_1 - \nu_2$
31343.9.....	1000	30900.3	760	443.6
31108.3.....	820	30755.1	460	443.2
31181.8.....	665	30737.5	305	444.3
Mean.....				443.7

Of course other differences of 444 units have been found, but none so convincing in significance as these above. Unfortunately, this interval does not seem to exist with any accuracy even between other pairs of less intense lines in these same groups.

Figure 2 gives an idea of the distribution of lines in the least refrangible part of the spectrum. In this region there are relatively wide intervals between successive lines so that analysis seems possible. Three series have been traced back into shorter wavelengths. They give evidence of reality, as may be judged from the data shown in Table II.

The first series in Table II is rather more satisfactory in its completeness and consistency than the other two. It is to be observed that the first few members of each series have a noticeably larger interval than the remaining members—a phenomenon not unusual in certain band spectra. The means of $\Delta\nu$ given above are computed with omission of these irregular intervals.

An attempt to extend the location of series which would consistently account for the majority of the lines measured has been fruitless. Apparently there are overlapping systems which the present resolution fails to disentangle. The proximity of successive lines necessarily makes selection of series members extremely uncertain.

TABLE II
POSSIBLE SERIES IN ABSORPTION-BAND SPECTRUM OF CS_2

ν	I	$\Delta\nu$	ν	I	$\Delta\nu$	ν	I	$\Delta\nu$
26896.0.....	I	289.2	26648.....	I	285.7	26497.....	I	291.0
27185.2.....	I	283.2	26933.7.....	I	292.3	26788.0.....	I	281.5
27468.4.....	I	273.8	27226.0.....	I	272.6	27069.5.....	I	288.7
27742.2.....	I	267.7	27498.6.....	I	277.9	27358.2.....	I	
28009.9.....	I	266.7	27776.5.....	I	265.7			2•268.8
28278.6.....	I	266.2	28041.2.....	I	267.0	27895.9.....	I	
28544.8.....	4	266.1	28308.2.....	I				2•264.0
28710.9.....	I	267.9			2•265.5	27424.0.....	4	264.0
28978.8.....	5	265.6	28839.1.....	16		27688.....	I	264.6
29244.4.....	12	267.2			3•267.1	27952.6.....	3	
29511.6.....	7	264.6						2•265.2
29776.2.....	23	266.3	29640.5.....	5	263.5	29483.1.....	20	
30042.5.....	23	265.8	29904.0.....	26	260.7			2•267.3
30308.3.....	58	267.9	30164.7.....	10	266.9	30017.8.....	15	264.5
30576.2.....	30		30431.6.....	33		30282.3.....	105	
.....		2•265.7			3•266.2			2•265.3
31107.6.....	680	264.3				30813.....	78	
31371.9.....	495	271.1	31230.1.....	36				2•265.4
31642.....	175	265.8			2•266.2	31343.9.....	1000	
31907.8.....	92	264.4	31762.5.....	230				3•265.7
32172.2.....	27				2•264.6			
.....		2•267.9	32291.6.....	170		32140.9.....	40	
32608.1.....	27	265.4			2•267.3			2•266.3
32873.5.....	68	262.4	32826.2.....	30	268.7	32673.5.....	10	
33135.9.....	43	268.2	33904.9.....	46				2•266.4
33404.1.....	53	267.2			2•265.8	33206.3.....	13	265.3
33671.3.....	13	265.1	33626.5.....	23	267.4	33471.6.....	10	
33936.4.....	10	266.9	33893.9.....	6	270.3			2•268.2
34203.3.....	5		34164.2.....	5		34008.1.....	2	
Means.....		266.4			266.1			266.0

Furthermore, owing to the incompleteness of the quantum theory of triatomic molecules, one does not know just what sort of relationships to expect. Doubtless, further empirical work together with more advanced theory will ultimately lead to a satisfactorily complete analysis.

In concluding, the writer wishes to express his thanks to Dr. Alpheus W. Smith for suggestion of the problem and for helpful advice and direction; also to the Physics Department for provision of the necessary facilities.

MENDENHALL LABORATORY
OHIO STATE UNIVERSITY
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ABSORPTION BAND SPECTRUM OF IODINE MONOCHLORIDE

BY

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ABSTRACT

Wave-lengths and series relations in the visible absorption spectrum of ICl.—The visible absorption spectrum of ICl has been photographed and measured. Eight new members have been located in the two series described by Gibson and Ramsperger as corresponding to $n''=1$ and $n''=2$. The limit of convergence of the former series is at $\nu=17430\pm5$ cm^{-1} , which makes the heat of dissociation equal to 49650 ± 15 calories per mol. Four members of a new series for which $n''=3$ have been found, so that it has been possible to compute the fundamental vibratory frequency of the molecule as 381.9 cm^{-1} . Still another series of five members is recorded, whose presence may be due to the existence of a close electronic doublet having a separation of about 36 cm^{-1} . The *ratio of the two specific heats* of gaseous ICl has been calculated to be 1.30 in agreement with empirical results. The *fine structure* of three consecutive bands has been measured, and the corresponding values of the parabolic parameter C have been computed to be in agreement with the theory of change of moment of inertia, I , with ω , the frequency of vibration of the molecule. By combining both sets of data for band heads and fine structure, the following approximate values for the *moment of inertia* have been computed: $I''=575\pm100\times10^{-40}$ $\text{g}\cdot\text{cm}^2$; $I'=995\pm200\times10^{-40}$ $\text{g}\cdot\text{cm}^2$.

INTRODUCTION

SINCE the experimental researches of Wood on the fluorescence spectrum of iodine and the interpretation of his results by Lenz in terms of quantum theory, attention has been focused upon the band spectra of molecules from the halogen group of elements. Further investigations of the molecular spectra of I_2 and also of Br_2 and Cl_2 , notably by Mecke and Kuhn, has led logically to new research upon the corresponding spectra of IBr and ICl. Because of its unusually high state of dissociation at ordinary temperatures, the absorption spectrum of IBr vapor has not yet been measured; but the more favorable monochloride has yielded definite results, its spectrum—in common with those of all the other halogen molecules—being situated in the red-to-green part of the visible spectrum and possessing one series which obviously converges to a definite limit.

Aside from preliminary work by Roscoe and Thorpe,¹ iodine monochloride has been investigated recently by Gibson and Ramsperger² and independently by the writer. It is felt that the present interest in the band spectrum of ICl warrants the presentation of somewhat more accurate measurements, which in addition to extending the series recorded by Gibson and Ramsperger and adding two new series, also include measurements of fine structure not made heretofore. The writer's investigation is therefore briefly outlined in the following.

¹ Roscoe and Thorpe, Phil. Trans. **167**, 207 (1876).

² Gibson and Ramsperger, Phys. Rev. **30**, 598 (1927).

TABLE I. Absorption band heads of ICl

λ (I. A.)	ν (vac.)	λ (I. A.)	ν (vac.)	λ (I. A.)	ν (vac.)	λ (I. A.)	ν (vac.)
5730.13	17446.9	5891.06	16970.2	6229.5	16048.2	6516.14	15342.3
69.4	328.0	5915.10	901.2	67.1	15951.9	44.36	276.1
73.23	316.6	41.31	826.9	68.8	947.6	88.00	174.9
78.7	300.1	70.62	744.0	82.78	912.1	6610.8	122.6
85.1	281.0	6002.97	16653.8	6315.0	830.9	63.96	002.0
92.90	257.7	38.7	555.3	24.92	806.1	82.3	14960.8
5801.8	232.7	78.12	447.9	38.83	771.4	6709.9	899.2
11.88	201.3	6120.63	333.7	6366.74	15702.3	57.6	794.1
23.72	166.5	34.9	295.7	85.06	657.3	81.3	742.4
37.5	125.9	66.33	212.6	6422.44	566.1	6836.80	622.7
53.04	080.4	80.66	175.0	48.57	503.0	56.35	581.0
70.82	028.7	6215.59	084.1	81.43	424.4	6920.8	445.2
		22.25	066.9			35.8	414.0

TABLE II. Fine structure of ICl bands at λ 6325, λ 6385 and λ 6449.

m^*	λ (I. A.)	ν (vac.)	m	λ (I. A.)	ν (vac.)	m	λ (I. A.)	ν (vac.)
0	6324.92	15806.1	?	6371.17	15691.4	55	6435.10	15535.5
15	29.04	795.8	53	72.16	88.9	?	40.39	22.7
16	29.58	94.5	54	73.94	84.6	?	41.53	20.0
17	30.04	93.3	55	75.72	80.2	58	42.67	17.2
18	30.67	91.7	56	77.42	76.0	60	46.40	08.2
19	31.27	90.2	57	79.34	71.3	?	49.04	01.9
20	31.88	88.7	0	85.06	57.2	0	48.57	03.0
21	32.64	86.8	?	89.67	45.9	19	54.83	488.0
22	33.27	85.3	?	90.40	44.1	20	55.48	86.4
23	34.08	83.2	23	93.93	35.5	21	56.13	84.9
24	34.91	81.2	24	94.70	33.6	22	56.78	83.3
25	35.61	79.4	25	95.52	31.6	23	57.55	81.4
26	36.42	77.4	26	96.34	29.6	24	58.28	79.7
27	37.43	74.9	27	97.17	27.6	25	59.12	77.7
28	38.19	73.0	28	98.13	25.3	26	59.89	75.8
29	39.23	70.4	29	98.99	23.1	27	60.85	73.6
30	40.18	68.1	30	99.93	20.9	28	61.68	71.6
31	41.24	65.4	31	6400.92	18.4	29	62.65	69.3
32	42.20	63.0	32	02.01	15.8	30	63.54	67.1
33	43.67	59.4	33	03.09	13.1	31	64.53	64.8
34	44.43	57.5	34	04.15	10.6	32	65.57	62.3
35	45.70	54.3	35	05.25	07.4	33	66.54	59.9
36	46.74	51.8	36	06.48	04.9	34	67.75	57.1
37	47.96	48.7	37	07.65	02.1	35	68.85	54.4
38	49.25	45.5	38	08.85	599.1	36	69.93	51.9
39	50.54	42.3	39	10.18	95.9	37	71.11	49.0
40	51.94	38.9	40	11.44	92.8	38	72.40	45.9
?	52.75	36.9	41	12.92	89.2	39	73.56	43.2
41	53.43	35.2	42	14.14	86.2	40	74.96	39.8
42	54.57	32.3	43	15.62	82.7	?	75.12	39.5
43	56.05	28.7	44	16.85	79.7	42	77.59	33.6
44	57.59	24.9	45	18.32	76.1	43	78.92	30.4
?	58.79	21.9	46	19.88	72.3	44	80.36	27.0
?	59.77	19.5	47	21.45	68.5	45	81.81	23.5
?	60.52	17.6	48	22.89	65.0	46	83.29	20.0
47	62.14	13.6	49	24.81	60.4	47	84.73	16.7
48	63.49	10.3	50	26.31	56.7	48	86.38	12.7
49	65.19	06.1	51	27.97	52.7	?	95.19	391.7
50	66.76	02.2	52	29.73	48.5	?	98.14	84.8
51	68.43	698.1	53	31.48	44.2			
52	70.13	93.9	54	33.38	39.6			

* Values of m assume $m=0$ at head and have no theoretical significance.

The wave-lengths of all observed band heads were measured from the plates by means of a low-power comparator. These measurements together with corresponding frequencies are recorded in Table I. The fine structure of three consecutive bands in the red was measured under much higher magnification. The resulting data are arranged in Table II.

ARRANGEMENT OF BAND SERIES

No attempt is made here to assign independently quantum values of n'' to the Deslandres' series, but the plausible assignments by Gibson and Ramsperger are adopted. However, their arbitrary assignments of n' are shifted one unit to admit a new member on the long wave-length end of the series $n''=2$. Table III shows specifically that six new members have been added to the converging series $n''=1$ and two new members to the weaker series $n''=2$. The series $n''=3$, consisting of four members is entirely new. Thus a value of 379.8 cm^{-1} is obtained for the second frequency interval in the normal group of energy levels in addition to the value of 381.2 cm^{-1} for the first interval.

EXPERIMENTAL PROCEDURE

Photographs were made in the first order on panchromatic plates with a 10-foot Rowland concave grating mounted in Eagle fashion. Continuous radiation, supplied by a 400-watt stereopticon bulb, was projected through ICl vapor contained in a tube of Pyrex glass, 60 cm long, with fused-on end plates of the same material. The vapor from pure ICl was admitted into the evacuated chamber at the center and was caused to progress slowly toward exhaust outlets near each end by proper adjustment of the pump. By this means the absorption spectrum of iodine as a dissociation product was reduced to a minimum. Exposures varied from 5 to 60 minutes. The iron arc was used for a comparison spectrum.

TABLE III. Series in band system of ICl

[illegible]

Fig. 1 is an energy level diagram including the new levels and showing the disposition of one of the new series.

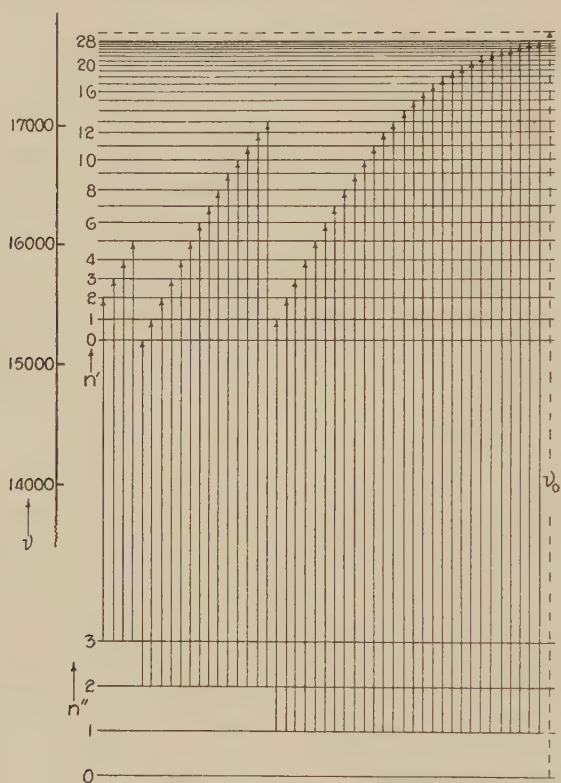


Fig. 1. Energy level diagram for the visible absorption spectrum of ICl.

Besides the heads classified in Table III, there remain out of Table I four additional ones which may be tabulated as follows:

ν	$\Delta\nu'$	$\nu(n''=1)$	$\Delta\nu'$	$\Delta\nu''$
15771.4	140.7	15806.1	141.5	34.7
15912.1	136.1	15947.6	135.7	35.5
16048.2	126.8	16084.1	128.5	35.9
16175.0	120.7	16212.6	121.1	37.6
16295.7		16333.7		38.0

wherein is included a member of the series $n''=2$. By comparison of $\Delta\nu''$'s it is seen that there is a rather good agreement between these and a similar group in Table III. There seems to be a real increase in the values of $\Delta\nu''$ together with the increase in ν . This would suggest an isotope effect, but the calculated displacement for this effect corresponding to $\nu=15806$ is 332 cm^{-1} , which is about ten times larger than the above values of $\Delta\nu''$.

This extra series may be due to the existence of an electronic doublet with a separation of about 36.3 cm^{-1} .

HEAT OF DISSOCIATION OF ICl

According to a method developed by Birge and Sponer,³ the frequency

³ Birge and Sponer, Phys. Rev. 28, 259 (1926).

at the limit of a convergent series for a non-polar molecule is given by

$$\nu_D = \nu_{n'} + \int_{n'}^{n'_0} \omega^{n'} dn',$$

where $\omega^{n'}$ is the frequency interval between $\nu_{n'}$ and $\nu_{n'-1}$, and n'_0 is the value of n' for which ω becomes zero. If $\omega^{n'}$ is plotted against corresponding values of n' (in which process $\omega^{n'}$ is to be considered as corresponding to n' rather than to $n'-1$ or the average of the two), the area under the curve

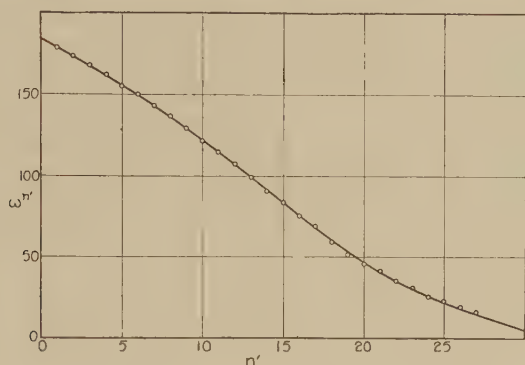


Fig. 2. Curve showing variation of $\omega^{n'}$ with n' .

is a numerical measure of the integral. Fig. 2 is such a curve plotted from Table III. The computed area is 2604.6 units when n' begins at zero. The extrapolated value of ν corresponding to $n'=0$ is 14825.4. Hence,

$$\nu_D = 14825.4 + 2604.6 = 17430.0.$$

The estimated error is about ± 5 units.

The heat of dissociation becomes

$$D = 2.152 \pm 0.001 \text{ volt} = 49650 \pm 15 \text{ calories per mol.}$$

The new frequency interval furnished by the series for $n''=3$ gives a means of computing ω_0'' , the fundamental frequency of the molecule in the normal state. For by fundamental theory,

$$\omega_0''(1-x'') = 381.2; 2\omega_0''(1-2x'') = 381.2 + 379.8 = 761.0.$$

Hence, solving $\omega_0'' = 381.9$ and $x'' = 0.0018$. Finally also, $\omega_0''x'' = 0.69$. Assuming that this law of convergence holds to the limit, it is easy to compute that the normal series of levels would converge at about the 278th level or about 82100 cm^{-1} from the zero state.

RATIO OF SPECIFIC HEATS

It has been shown by Planck⁴ that if ν is the fundamental frequency of vibration of a diatomic molecule, the specific heat at constant volume is given by the equation

$$\frac{C_v}{R} = \frac{5}{2} + \frac{x^2 e^x}{(e^x - 1)^2},$$

⁴ Planck, *La Theorie du Rayonnement et les Quanta*, p. 112 (1911).

in which x has been used as an abbreviation for $h\nu/RT$. For a temperature of 100°C , $x=1.466$.

Hence, $C_v/R=3.33$, and $C_p/R=1+C_v/R=4.33$. Therefore, $C_p/C_v=\gamma=1.30$. This value is in close agreement with the mean value 1.31 determined experimentally by Strecker⁵ for γ at the same temperature.

DISCUSSION OF FINE STRUCTURE

Even a casual glance at Table II reveals that the fine structure must be of a simple nature. Aside from an occasional extra line, the measurements consist of three parabolic series corresponding to the three bands heading respectively at 6325, 6385 and 6449A. Fig. 3 is a curve plotted from the data

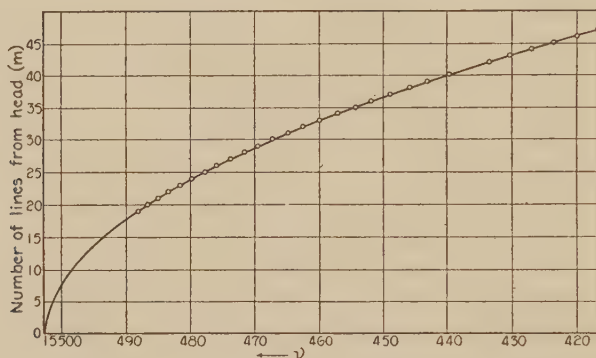


Fig. 3. Typical parabolic curve for fine structure.

for the latter band. The curve has been extended to tangency at the head according to a parabolic law. The data for the other two bands yield exactly similar curves. Unfortunately there is no definite indication of the presence of the null lines, and hence it is impossible to evaluate the frequency interval at the origin, which is necessary to a computation of moment of inertia. However, certain quantitative results may be definitely secured.

In evaluating the constant C of the general band formula, it is immaterial whether the measured lines belong to a P , Q , or R branch, for C is nearly identical for all three types.

For sake of definiteness, let us set for the frequency of any line of the branch in a band $\nu_1=A-2Bm_1-Cm_1^2$. Any other line in the same branch will be given approximately by $\nu_2=A-2Bm_2-Cm_2^2$. Subtracting, $\nu_1-\nu_2=(m_2-m_1)[2B+C(m_2+m_1)]$. Let $m_2-m_1=10$. Then, $\nu_1-\nu_2=20[B+C(m_1+5)]$. Similarly, if we set $m_3-m_1=20$, $\nu_1-\nu_3=40[B+C(m_1+10)]$. Both B and m_1 may be readily eliminated so that one obtains $100C=\nu_2-(\nu_1+\nu_3)/2$ where ν_1 , ν_2 and ν_3 are the frequencies of lines ten intervals apart in order. This is a very convenient equation for determination of C , and shows that analytically C is a measure of the difference between any frequency and the average value of two frequencies symmetrically situated on either

⁵ Strecker, Wied. Ann. 17, 93 (1882).

side. Applying this equation to all possible sets of lines in the three bands, the mean values of C obtained for each band were:

Band Head	15503.0	15657.2	15806.1
C	0.0388	0.0398	0.0412

The physical significance of C as taken here is given by the identity

$$C \equiv \frac{h}{8\pi^2 c} \left[\frac{1}{I''} - \frac{1}{I'} \right],$$

where I' is the moment of inertia in the excited state, and I'' that in the normal state. Comparing values of C for the different bands, it can be readily observed that the value of I' increases as one proceeds toward the limit of the series. This is in agreement with the established correlation between I and ω (the vibrational frequency) which are consistently found to be roughly in inverse proportion. By approximate extrapolation, C becomes 0.035 for $n' = 0$ as assigned.

MOMENT OF INERTIA

An approximation to the value of the moment of inertia of ICI can be obtained if it is assumed that the assignments of n' are nearly correct. For Mecke⁶ has pointed out that the product of the mean value of ω by the mean value of the moment of inertia is nearly equal to the product $\omega'' I''$. Or, $(178 + 382) (I' + I'')/2 = 382 I''$; whence, $I' = 1.73 I''$. Also

$$C = \frac{h}{8\pi^2 c} \left[\frac{1}{I''} - \frac{1}{I'} \right] = 0.035.$$

Solving these two equations simultaneously,

$$I'' = (575 \pm 100) 10^{-40} \text{ g} \cdot \text{cm}^2;$$

$$I' = (995 \pm 200) 10^{-40} \text{ g} \cdot \text{cm}^2.$$

As indicated, these results may be in error by as much as twenty percent.⁷

In conclusion, the writer wishes to express his thanks to Professor Alpheus W. Smith who originally suggested the problem and whose personal interest has been a strong incentive throughout the investigation.

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May, 1928.

⁶ Mecke, *Zeits. f. Physik* **32**, 823 (1925).

⁷ If we assume momentarily that the extra series tabulated below Table III might be the heads of Q branches belonging to the nearest strong band, a position for the null line of the band at $\nu = 15806$ would be determined. Under this assumption, the value of the constant B turns out to be 1.195; whence, $I' = 23.1 \cdot 10^{-40} \text{ g} \cdot \text{cm}^2$. This result is only two or three percent. of the approximate value obtained above by another method, and hence we dismiss the possibility of the extra series, being accounted for by Q branches.

TEMPERATURE OF THE UNDER-WATER SPARK AS COMPUTED FROM DISTRIBUTION OF INTENSITY IN OH ABSORPTION BANDS

BY EARL D. WILSON

ABSTRACT

Detailed measurements of the OH-bands found absorbed in the under-water spark reveal that the system is developed in absorption almost as completely as in emission. Calculations based on intensity distribution lead to a value of approximately 5000°C for the effective temperature of the source.

INTRODUCTION

The strong "water band" at $\lambda 3064$, now ascribed to the carrier OH, was discovered in emission in 1880. Credit for the discovery is shared in the literature between Huggins¹ and the pair of investigators Liveing and Dewar,² who later examined the whole band system in the ultra-violet. The accurate and extensive measurements of wave lengths for the band at $\lambda 3064$ made in 1912 by Grebe and Holtz,³ were used by Heurlinger⁴ in 1918 for quantum analysis. Heurlinger succeeded in arranging almost all of Grebe and Holtz's lines into twelve parabolic series, forming two distinct bands of three double branches each. The stronger band headed at $\lambda 3064$, while the weaker headed at $\lambda 3126$ (less refrangible R-branch).

Six years later Watson⁵ measured and analyzed in an exactly similar manner the band $\lambda 2811$ together with its weaker neighbor at $\lambda 2875$. Finally in 1927 Jack⁶ measured and classified the lines of the band at $\lambda 2608$. The additional experimental and theoretical work of other investigators leave little to be desired with respect to the analysis of the band system in emission, and altogether make it quite probable that the carrier is OH.

That the OH-bands occur also in absorption under various conditions is very well known. We may refer to the work of Deslandres,⁷ of Liveing and Dewar,⁸ and of Fowler⁹ on the presence of "water

¹ Huggins, *Proc. Roy. Soc.*, 30, p. 576; 1880.

² Liveing and Dewar, *Proc. Roy. Soc.*, 30, p. 494; 1880.

³ Grebe and Holtz, *Ann. d. Phys.*, 39, p. 1243; 1912.

⁴ Heurlinger, *Dissertation*, Lund, 1918.

⁵ Watson, *Astrophys. Journ.*, 60, p. 145; 1924.

⁶ Jack, *Proc. Roy. Soc.*, 115, p. 373; 1927.

⁷ Deslandres, *Comptes Rendus*, 100, p. 854; 1885.

⁸ Liveing and Dewar, *Phil. Trans.*, 179, p. 27; 1888.

⁹ Fowler, *Proc. Roy. Soc.*, 94, p. 472; 1917-18.

bands" in absorption in the solar spectrum; or to the work of Hulthen and Zumstein¹⁰ on the ready absorption of the band at $\lambda 3064$ by the oxyhydrogen flame. More than twenty-five years ago Konen¹¹ mentioned the reversal of the "water bands" in the under-water spark; and during the last quarter of a century many investigators who have employed the under-water spark as a source of continuous radiation in the ultraviolet have reported more or less incidentally the presence of these bands in absorption in the source.

It has been the purpose of the writer, first, to measure all the lines appearing in the under-water source in order to ascertain how fully the bands are developed in such absorption; and, secondly, to measure in so far as possible the intensities of the lines in the various branches. Since Birge¹² has been successful in relating the distribution of intensity in band spectra to the temperature of the source in a rather simple manner, it is hoped that it might be possible to compute from such measurements of intensity the effective temperature of the under-water spark.

SPECTROGRAPHIC PROCEDURE

The electrical circuit employed to produce the under-water spark is outlined in Fig. 1. The energy was supplied from 110-volt, A.C. mains through a ballast resistance to the primary of a $2\frac{1}{2}$ k.v.a. trans-

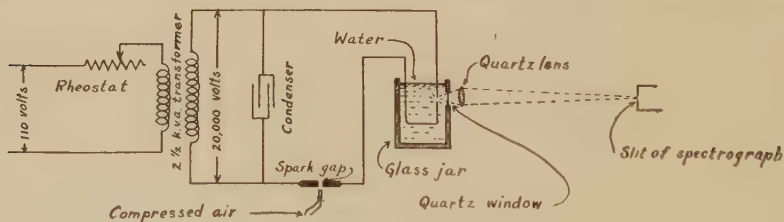


FIG. 1. Diagram of apparatus

former. The secondary, at a tension of 20,000 volts, charged a large condenser which in turn produced a high-frequency oscillatory discharge through an external auxiliary spark gap and an under-water gap in series. The auxiliary gap, about 1 cm in length, was quenched by means of a strong continuous blast of air. For the under-water gap aluminum electrodes, 5 mm in diameter, were employed. They were provided with wedge-shaped terminals whose edges were oriented so

¹⁰ Hulthen and Zumstein, *Phys. Rev.*, 28, p. 13; 1926.

¹¹ Konen, *Ann. d. Phys.*, 9, p. 742; 1902.

¹² Birge, *Astrophys. Journ.*, 55, p. 273; 1922.

as to lie parallel to the axis of collimation. The distance between the terminals was of the order of 1 mm.

The medium for the spark was tap water in slow circulation. It was contained in a glass jar provided with a quartz window before which was permanently attached a small quartz condensing lens of diameter 2.5 cm, and focal length 5 cm. This single lens was so situated as to project upon the slit of the spectrograph a magnified image of the source just large enough to fill the exposed part of the slit (3mm) with ultraviolet light, and yet not large enough to dissipate the energy transferred.

The spectrograph, made by Hilger, was of the E-1 type, having a dispersion of about 5.3A per mm at $\lambda 3064$ and about 3.9A per mm at $\lambda 2811$. It was focused for the region from $\lambda 2600$ to $\lambda 4000$. The slit width was adjusted to 3 divisions from the actual zero.

Since the absorbing medium lay in the source itself, the taking of the pictures was comparatively simple. In accordance with the usual practice, the spectrum of an iron arc was photographed above and below each spectrum from the under-water source. Length of exposures for the latter ranged from 1 sec. to 10 min. The plates selected for measurement were simply those which under microscopic examination revealed the sharpest structure for the OH-bands.

PHOTOMETRIC PROCEDURE

No direct measurements of wave length were made from the plates, but from intensity curves traced by a Moll microphotometer. To secure photometer records from which measurements both of wave lengths and intensities could be made, a select plate was adjusted in the instrument so that the band structure would traverse the incident beam, and the trace was completed in the usual manner. Then the instrument being returned to its initial position, a trace for the comparison emission spectrum of iron was registered on the same strip of sensitized paper. The result was that the systems of absorption and emission lines extended toward each other, frequently being quite adjacent at their peaks.

MEASUREMENTS OF WAVE LENGTHS

A special form of comparator fitted with a low-power objective was employed to measure the wave lengths of the absorption lines directly from the photometric prints by comparison with the iron lines. A graphical method of interpolation reduced scalar readings to Angstrom

units and automatically corrected for prismatic curvature on the plate and the possible lateral displacement of the plate during the photometric process.

DESCRIPTION OF RESULTS

The measurements revealed the presence of all the double branches in Watson's bands at $\lambda 2811$ and $\lambda 2875$ as well as all the double branches in Heurlinger's bands at $\lambda 3064$ and $\lambda 3126$.

By comparison with Watson's data (employing conventional notation) all the members of the R_1 branch of band $\lambda 2811$ from $m=2$ to $m=19$, inclusive, were identified, only members 5 and 12 being doubtful. Also in the R_2 branch, members from quantum number 2 to number 19 were all found. In the Q_1 branch, lines 2 to 22 were all identified but number 23 could not be located. The Q_2 branch contained every one of the lines from $m=2$ to $m=22$, a twenty-third line not being listed in emission. Of the lines in the P_1 branch, those from $m=2$ to $m=21$ were identified, the twenty-second not being found. The presence of members 4 and 21 was rather doubtful. Similarly, in the P_2 branch, lines 2 to 21 were found, the twenty-first being doubtful and the twenty-second not being located.

In the weaker band at $\lambda 2875$, the R_1 branch yielded lines $m=5, 6, 8$ out of Watson's 4 to 8 inclusive, number 5 being doubtful, and 6 and 8 coincident; but the R_2 branch contained all the listed members 4 to 8. In each of the branches Q_1 and Q_2 all the lines from $m=2$ to $m=11$ were identified. In the P_1 branch, member 5 was doubtful, while all the remaining ones from 2 to 12 were definitely located. The P_2 branch yielded all the listed lines from 2 to 11, but lines 3 and 6 were uncertain.

Now for these two bands in the spectral region of shorter wave lengths, the dispersion was happily adequate to a practically complete separation of lines. However, in Heurlinger's bands at $\lambda 3064$ and $\lambda 3126$, the dispersion was less, and consequently lines were sometimes unresolved, making the identification more difficult.

In the strong band at $\lambda 3064$, out of Heurlinger's listed lines $m=2$ to $m=25$ for the R_1 branch, seventeen were identified. Numbers 2, 19, 20 and 22 were concealed by two strong aluminum absorption lines. Numbers 6, 7, and 11 were too near stronger lines to be resolved. We add also that the measurements of lines 10, 12, 13, 23 and 25 (as in the case of certain other lines in this band) were somewhat inaccurate because of lack of resolution. In the R_2 branch, lines 4 to 22 were found, but numbers 2, 3, 10 and 21 were unresolved, and number 20 was hidden

by an aluminum line. The Q_1 branch contained the listed lines from $m=2$ to $m=29$, except that number 26 was not found, and lines 14, 17 and 29 were doubtful. In the Q_2 branch, aside from four concealed lines, all members were identified except the last three, and line 15 was uncertain. In the P_1 and P_2 branches, which ran out to the longest wave lengths, lines 24 to 28 could not be definitely located because of faintness. In the latter branch also line 8 was not found.

For the weaker band at $\lambda 3126$ (head of R_1 branch), lines 5, 7, 8 and 9 were not found in the listed lines from $m=5$ to $m=14$ in the R_1 branch. Of the eight lines (at least) belonging to the R_2 branch, which Heurlinger did not analyze, six were identified from Grebe and Holtz's measurements. In the Q_1 branch, all the lines were found from $m=3$ to $m=20$ except numbers 5, 12, 13, 16, 19, and 20. Out of the 19 listed lines for the Q_2 branch, only lines 2, 6, and 14 could not be found. The P_1 branch yielded nine lines out of fifteen, but again in the P_2 branch all members were identified from $m=2$ to $m=17$ as listed except numbers 5, 7 and 13. Also lines 16 and 17 were uncertain.

As a summary of the results of the line measurements, the following statements may be clarifying. Watson records 121 lines for the band at $\lambda 2811$. Of these lines 113 have been identified with possibly 5 more lines doubtful. For the weak band at $\lambda 2875$ Watson measured 51 lines. Of this band 45 lines have been found in absorption, with possible addition of 4 doubtful ones. For the band at $\lambda 3064$, of the 145 lines classified by Heurlinger which lay within the range of wave lengths contained on the print, 139 were either directly identified or accounted for in unresolved lines, with 3 additional doubtful ones. In the weak band at $\lambda 3126$ (head of the R_1 branch there were found 64 of the 76 lines listed by Heurlinger, with possibly 2 more. Of the total 247 lines in both bands measured by Grebe and Holtz in the range investigated in this paper, 222 were identified, 3 more being doubtful. It is interesting to note that several of the lines either not accounted for or not found at all on the prints are not tabulated in Heurlinger's classification of the branches, but are included in the complete tables of Grebe and Holtz.

As an illustration of the completeness of development of the branches in absorption, and to gauge the order of accuracy involved in the measurements, we append the following table for the Q branches of Watson's band at $\lambda 2811$.

In these forty-two measurements, the largest single deviation from

TABLE 1. *Comparison of lines measured in absorption with those measured in emission band at $\lambda 2811$*

Branch Q ₁				Branch Q ₂			
m	λ (I. A.) Watson	λ (I. A.) Writer	$\Delta\lambda$	m	λ (I. A.) Watson	λ (I. A.) Writer	$\Delta\lambda$
2	2829.25	2829.23	-0.02	2	2819.13	2819.19	+0.06
3	28.95	28.93	- .02	3	20.66	20.64	- .02
4	29.35	29.34	- .01	4	22.39	22.44	+ .05
5	30.31	30.28	- .03	5	24.37	24.43	+ .06
6	31.81	31.80	- .01	6	26.65	26.62	- .03
7	33.82	33.77	- .04	7	29.25	29.23	- .02
8	36.30	36.32	+ .02	8	32.20	32.17	- .03
9	39.21	39.21	.00	9	35.51	35.49	- .02
10	42.62	42.60	- .02	10	39.21	39.21	.00
11	46.45	46.41	- .04	11	43.27	43.22	- .05
12	50.72	50.71	- .01	12	47.75	47.78	+ .03
13	55.43	55.42	- .01	13	52.65	52.67	+ .02
14	60.60	60.59	- .01	14	57.96	57.93	- .03
15	66.23	66.30	+ .07	15	63.71	63.70	- .01
16	72.32	72.26	- .06	16	69.90	69.91	+ .01
17	78.87	78.86	- .01	17	76.55	76.54	- .01
18	85.91	85.92	+ .01	18	83.69	83.70	+ .01
19	93.47	93.44	- .03	19	91.29	91.31	+ .02
20	2901.54	2901.48	- .06	20	99.42	99.42	.00
21	10.05	10.02	- .03	21	2907.99	2908.04	+ .05
22	19.18	19.20	+ .02	22	16.92	17.00	+ .08
23	28.88						

Watson's values is 0.08 Angstrom, and this difference is for a very faint line. The average of the absolute values of $\Delta\lambda$ is 0.03. This value may fairly be taken as the order of accuracy to be expected in the measurements described.

MEASUREMENTS OF INTENSITY

The law of photographic blackening together with the empirical results of G. R. Harrison¹³ on the characteristics of panchromatic emulsions leads rather directly to a simple approximation formula for the intensity of weak lines in absorption, namely

$$I = k \frac{a}{d^2},$$

where a is the small area enclosed by an absorption peak on the photometer print, d is the total displacement from zero of the galvanometer

¹³ G. R. Harrison, J.O.S.A. & R.S.I., 11, p. 341; 1925.

trace on the print for the given peak, and k is a constant of proportionality. The specification of the area enclosed by the peak naturally implies that each line whose intensity is to be measured is distinct from other lines so that there is no overlapping of areas. Unfortunately, this restriction is not generally satisfied in the OH-bands under experimental conditions. Although the band at $\lambda 2811$ most nearly approaches complete separation of lines, its faintness made the value of a too small to be measured with any certainty. The strongest band at $\lambda 3064$ provided measureable values of a , but the dispersion, was not quite adequate to a generally complete separation of lines. By comparing the observed wave lengths of all the peaks on the photometric print belonging to this band with Heurlinger's classification, and checking off those peaks which represented either actual coincidences or unresolved groups, it was discovered that the P_2 branch alone possessed a sufficient number of "free" (or nearly "free") lines to determine an intensity curve. The Q_1 branch afforded a less satisfactory set of six lines, while the P_1 branch afforded only four scattered lines. Table 2 gives the computed values of I in arbitrary units.

TABLE 2. *Intensities of certain absorption lines in the band at $\lambda 3064$*

Branch P_1			Branch P_2			Branch Q_1		
m	I	λ (I. A.)	m	I	λ (I. A.)	m	I	λ (I. A.)
3	95	3096.34	5	129	3096.12	8	180	3094.61
12	128	3140.72	6	151	3101.22	12	346	3105.65
15	53	61.88	10	257	24.92	13	287	09.32
17	54	77.67	11	249	30.24	18	125	33.20
			12	200	36.87	19	66	39.14
			13	133	43.77	25	16	83.91
			14	100	50.98			
			16	67	66.32			
			18	51	82.95			
			20	31	3200.94			

THEORETICAL INTERPRETATION

Birge¹⁴ reports that for simple types of band spectra the intensity in each branch is distributed in such a way as to satisfy the empirical relation

$$\text{intensity} = me^{-am^2}$$

where m is the whole rotational quantum number for a given line and a is a parameter evidently depending on J , the moment of inertia, and

¹⁴ Birge, *Molecular Spectra in Gases*, p. 155; 1927.

on T , the absolute temperature. This empirical relation is the same as that deduced by Kemble¹⁵ from classical theory. By inserting the expression

$$E_m = \frac{m^2 h^2}{8\pi^2 J}$$

for the energy of rotation into Maxwell's distribution function and combining with the above equation, there results

$$\text{Intensity} = cm e^{-m^2 h^2 / 8\pi^2 J k T}$$

By differentiating with respect to m and equating to zero,

$$m_{\max} = \frac{2\pi}{h} (kJT)^{1/2}$$

or,

$$T = \frac{h^2}{4\pi^2 kJ} m_{\max}^2,$$

which states that the effective temperature of the source is, for a given type of molecule, determined by the whole rotational quantum number of the line in a branch which has maximum intensity. Recalling that h is Planck's constant (6.55×10^{-27}) and k is the molecular gas constant (13.72×10^{-17}), our equation reduces to

$$T = 79.2 \times 10^{-40} \frac{m_{\max}^2}{J}.$$

Fig. 2 is a graphical representation of the central columns of Table 2, the intensity being plotted against corresponding quantum numbers of the P_2 branch. There is no doubt that a maximum exists in the neighborhood of $m=10$, and is apparently at about $m=10.2$. The data for the other two branches, although not decisive, are of such a nature as to corroborate this result.

There remains yet the value of J to be inserted into the formula. In the theory this moment of inertia is assumed to be constant during an absorption process. Birge's¹⁶ tables give for the initial J in emission for the OH carrier with respect to the band at $\lambda 3064$,

$$J' = 1.63 \times 10^{-40}$$

¹⁵ Kemble, Phys. Rev., 8, p. 689; 1916.

¹⁶ Birge, Molecular Spectra in Gases, p. 232; 1927.

and for the final J in emission

$$J'' = 1.43 \times 10^{-40}.$$

Hence we take the average value, $J = 1.53 \times 10^{-40}$ for our computations. Thus

$$\begin{aligned} T &= \frac{79.2 \times 10^{-40}}{1.53 \times 10^{-40}} \cdot (10.2)^2 \\ &= 5387^\circ \text{ Abs.} \\ &= 5115^\circ \text{ C, approximately} \end{aligned}$$

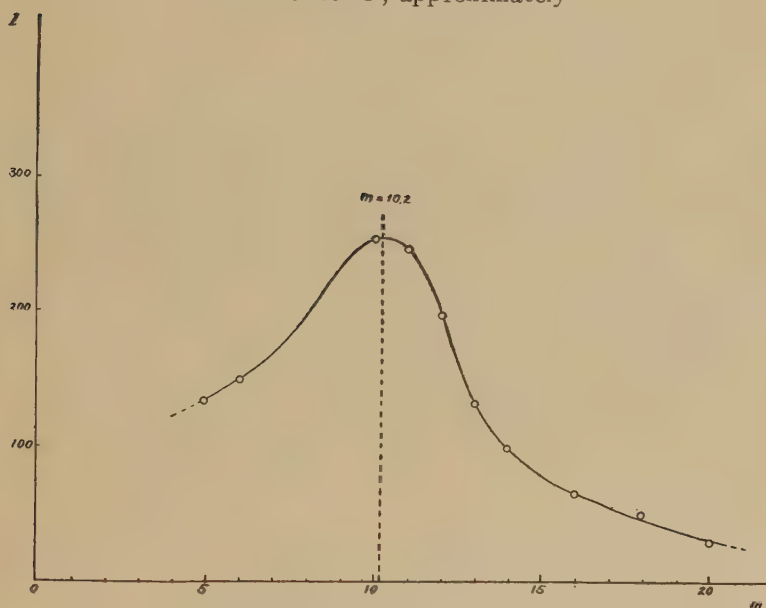


FIG. 2. Curve showing intensities of lines in P_2 branch of band at $\lambda 3064$.

It is not unreasonable to expect a very high temperature in the under-water spark, when one considers the spectroscopic data. The OH-bands have the assigned vibrational quantum numbers as follows: $\lambda 3064 = 0, 0$; $\lambda 3126 = 1, 1$; $\lambda 2811 = 1, 0$; $\lambda 2875 = 2, 1$. Under ordinary conditions of absorption one should expect to find only those bands which correspond to transitions of vibrational energy from the normal vibrationless state ($n'' = 0$) to higher quantum states. This would produce the strong band $\lambda 3064 (0, 0)$ and the weaker band $\lambda 2811 (1, 0)$. The fact that our data show that also bands $\lambda 3126 (1, 1)$ and $\lambda 2875 (2, 1)$ occur, certainly indicates that the temperature of the carrier OH in the source was great enough to cause an appreciable fraction of them to be in the first vibrational quantum state.

SUMMARY

1. Measurement of the wave lengths of lines observed in the OH-bands absorbed in the under-water sparks shows that the bands at $\lambda 2811$, $\lambda 2875$, $\lambda 3064$ and $\lambda 3126$ are developed almost as fully as in emission.

2. Measurement of intensity in branches of the bands at $\lambda 3064$ reveals a maximum at about $m = 10.2$, from which value the effective temperature of the under-water spark has been computed from Birge's formula to be 5115°C under the existing experimental conditions.

3. Since the data indicate that a rather high temperature is to be expected in the under-water spark, the results may be considered as an empirical check upon the validity of the formula.

The writer wishes to express his indebtedness to Professor Raymond T. Birge of the University of California for assistance in calculating the effective temperature of the spark and to Professor Alpheus W. Smith who suggested the problem and gave valuable aid in the solution.

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AUTOBIOGRAPHY

I, Earl DeWitt Wilson, was born at Derthick, Ohio, on March 7, 1898. My secondary education was received in the public schools at Roseville, Ohio. I obtained the Degree of Bachelor of Arts from Capital University, where I was graduated in 1919. Further classical and science courses were pursued at the same institution for two years. The Degree of Master of Arts was secured at the Ohio State University in 1923. Three years were then spent as instructor in Physics at Capital University. In 1928 I received from the Ohio State University the Degree of Doctor of Philosophy.

